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The PM_{10} Fraction of Road Dust in the UK and India: Characterization, Source Profiles and Oxidative Potential

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ABSTRACT

Most studies of road dust composition have sampled a very wide range of particle sizes, but from the perspective of respiratory exposure to resuspended dusts, it is the PM_{10} fraction which is of most importance. The PM_{10} fraction of road dust samples was collected at two sites in Birmingham, UK (major highway and road tunnel) and one site in New Delhi, India. Dust loadings were found to be much higher for New Delhi compared to Birmingham, while concentrations of several species were much higher in the case of Birmingham. Detailed chemical source profiles were prepared for both cities and previously generated empirical factors for source attribution to brake wear, tyre wear and crustal dust were successfully applied to the UK sites. However, 100% of the mass for the Indian site could not be accounted for using these factors. This study highlights the need for generation of local empirical estimation factors for non-exhaust vehicle emissions. A limited number of bulk road dust and brake pad samples were also characterized. Oxidative Potential (OP) was also determined for a limited number of PM_{10} and bulk road dust samples, and Cu was found to be a factor significantly associated with OP in PM_{10} and bulk road dust.

Keywords: Non-exhaust emissions; source profile; source apportionment; road dust; Oxidative Potential

1. INTRODUCTION

Emissions from road vehicles are of importance for human health as they are emitted in the vicinity of human activity, and street canyon effects can enhance pollutant levels by limiting dispersion (Colville et al., 2001). Particulate matter (PM) emissions from road vehicles include both exhaust and non-exhaust (wear and tear of vehicle parts, resuspension of dust) constituents (Pant and Harrison, 2013). Non-exhaust emissions are more abundant in the coarse size fraction (particles with aerodynamic diameter of 2.5-10 μm) and can deposit on the roadside and be resuspended subsequently due to vehicle activity. Road dust (RD) consists primarily of coarse-sized PM derived from different sources such as wear of vehicle components (brakes, tyres and clutches), the road surface, engine corrosion, tailpipe emissions, crustal dust and other emission sources. However, similarity in composition between direct emission sources such as brake wear and tyre wear and particles resuspended from the road surface renders it difficult to distinguish the contribution of the different sources (Bukowiecki et al., 2010). RD can be a significant source of trace metals, particle-bound polycyclic aromatic hydrocarbons (PAHs) and other chemical species in the atmosphere (Amato et al., 2009; Duong and Lee, 2011; Kwon and Castaldi, 2012). Several studies on RD have reported elemental and organic marker concentrations for RD in different size fractions (Han et al., 2007; Morillo et al., 2007; Agarwal, 2009; Amato et al., 2009; Faiz et al., 2009; Duong and Lee, 2011; Gunawardana et al., 2011; Martuzevicius et al., 2011). Crustal dust is characterized by elements such as Si, Al, Ti, Mn and Fe while non-exhaust emissions are typically characterized by trace metals such as Cu, Ba, Sb, Sn (brake wear) and Zn (tyre wear) (Wahlin et al., 2006; Gietl et al., 2010; Hulskotte et al., 2014). However, several authors have also used organic markers (e.g. PAHs, n-alkanes, benzothiazoles) as source tracers (Lough et al., 2005; Kwon and Castaldi, 2012). Enrichment of both trace elements and organic species has been reported in RD compared to background soils worldwide (Han et al., 2007; Liu et al., 2007; Agarwal, 2009; Duong and Lee, 2011; Luo et al., 2011; Peltier et al., 2011). Elements such as Pt, Pd and Rh have also

been reported to be present in RD and are attributed to emissions from catalytic converters (Prichard and Fisher, 2012).

It is important to note that the chemical source profile (i.e. percentage of species with respect to total PM mass) for contaminated soil as well as non-exhaust emissions varies geographically dependent upon parameters such as traffic (volume and pattern, fleet characteristics), and road surface type, and the climate and geology of the region (Omstedt et al., 2005; Amato et al., 2011; Pant and Harrison, 2013; Kwak et al., 2013). Most of the research, as well as policy action, in the last few decades has focused largely on exhaust emissions, and with a decline in percentage contribution of vehicle exhaust emissions to ambient PM, the contribution of non-exhaust PM is of increasing importance (Thorpe and Harrison, 2008; Denier van der Gon et al., 2013). Detailed accounts of sources and properties of non-exhaust emissions and ambient measurements of non-exhaust components are provided elsewhere (Luhana et al., 2004; Thorpe and Harrison, 2008; Pant and Harrison, 2013; Amato et al., 2014). Typical methods for characterization of RD and non-exhaust emissions include use of a brake dynamometer (Garg et al., 2000), rolling resistance testing machine (Rogge et al., 1993), rotating drum method (Camatani et al., 2001), sweep/vacuum collection of particles followed by sieving or resuspension (Duong and Lee, 2011; Martuzevicius et al., 2011) and use of a specific RD sampler (Amato et al., 2009). Several researchers have analysed the chemical composition of brake components (Rogge et al., 1993; Garg et al., 2000; Kukutschova et al., 2010, 2011; Hulskotte et al., 2014) and tyres (Camatani et al., 2001; Adachi and Tainosho, 2004; Councell et al., 2004; Milani et al., 2004; Aatmeeyata and Sharma, 2010).

Much of the reported research has been conducted on bulk or very coarse fractions of RD, with a very few studies focused on the characterization and source apportionment of the PM_{10} fraction of RD (Wahlin et al., 2006; Amato et al., 2009; Han et al., 2009; Amato et al., 2011). In order to quantify RD as a source of airborne PM, it is important to prepare detailed chemical source

93 profiles. Both India and UK lack detailed chemical source profiles for the RD source. For New
94 Delhi, source profiles for PM_{10} RD (paved, unpaved and soil) were published as a part of a
95 larger study but the molecular markers were not analysed in detail (Sethi and Patil, 2008).

96

97 The aims of this study were to characterize the chemical composition of the PM_{10} fraction RD, to
98 prepare a PM_{10} RD source profile and to calculate the contribution of non-exhaust emission
99 sources to samples of RD in Birmingham (UK) and New Delhi (India). In addition, Oxidative
100 Potential of the RD samples from the UK was assessed. To the best of our knowledge, this is the
101 first study to undertake detailed elemental as well as molecular marker and oxidative
102 characterization of the PM_{10} fraction of RD either in India or the UK.

103

104 **2. METHODS**

105 **2.1 Sampling Sites**

106 Samples were collected at two high traffic locations in Birmingham: Bristol Road- a heavily
107 trafficked road (hereafter referred to as Site A) and Queensway A38 tunnel – a road traffic tunnel
108 (hereafter referred to as Site B) and one heavily trafficked site in New Delhi: Mathura Road-
109 NH2 (hereafter referred to as Site C). Site A (UK roadside) is one of the major arterial roads in
110 south-west Birmingham with a dual carriageway with 32,000 vehicles/day and includes both
111 gasoline and diesel vehicles. RD samples were collected on both sides of the road close to the
112 traffic junction. Site B (UK road tunnel) is one of the major road tunnels in Birmingham and
113 runs in the North/South direction. The tunnel is naturally ventilated and typical driving speed
114 through the tunnel is 30 miles/hour with an estimated 89,000 vehicles travelling each day. Several
115 studies have been conducted at both these sites in the past (Smith and Harrison, 1996; Birmili et
116 al., 2006). Site C (India roadside) is one of the major roads in Delhi and falls on the National
117 Highway 2. An estimated 174,200 vehicles per day run on this road including intra-state and interstate

traffic. Public transport (including buses and auto-rickshaws) runs on compressed natural gas (CNG) while personal vehicles run on both gasoline and diesel. Figure S1 (SI) provides the modal split at the various sites (Azzi, 2012; DoT, 2014; Pant et al., 2015).

2.2 Sampling

A custom-built PM_{10} dust sampler (as described in Amato et al., 2009) was used to collect the RD samples. Samples were collected onto 47 mm PTFE and quartz fibre filters to enable analysis of elements and organic species. Both PTFE (n=10) and quartz filter (n=10) samples were collected at Sites A and C (UK and India roadside) while only PTFE filter samples (n=10) were collected at Site B (UK tunnel). All the samples were collected after five days of dry weather in September 2012 (Site B) and June-July 2013 (Sites A and C- UK and India roadside). Individual samples were collected over an area of $1m^2$ for a period of 15 minutes and include samples from the kerbside as well as middle of the road.

In spring 2014, soil, bulk RD, brake pad and tyre samples were collected in Birmingham while soil and brake pad samples were collected in India in June 2014. The soil samples were collected from the lawns of University of Birmingham and the CRRI campus remote from traffic in Birmingham and New Delhi respectively while the brake pads were sourced from local garages. Only one brake pad per city was analysed. Care was taken to ensure that the soil samples were collected from an uncontaminated area. An additional set of PM_{10} RD samples were also collected at Site A (UK roadside). The soil and RD samples were dried, ground using a pestle and mortar and sieved using a 2 mm sieve; 0.5 g of each sample was then extracted and analyzed using the methods detailed in the next section. Brake pad (UK and India) and tyre (UK) samples were frozen using liquid nitrogen (N_2) and subsequently ground. The samples were passed through a 2 mm sieve and extracted and analyzed.

2.3 Chemical Analysis

Details of the analytical procedures are provided in the SI.

3. RESULTS AND DISCUSSION

3.1 Mass Loadings of PM_{10} RD Fraction

Average PM_{10} mass loading on the road surface was found to be much higher in New Delhi compared to Birmingham: 9.34 ± 5.56 mg/m^2, 12.1 ± 9.3 mg/m^2 and 72.9 ± 24.3 mg/m^2 for sites A (UK roadside), B (UK road tunnel) and C (India roadside) respectively. Mass loadings varied between 3.78- 21.8 mg/m^2, 3.01-36.1 mg/m^2 and 44-106 mg/m^2 at Sites A, B and C respectively. In comparison, an average mass loading of 9 mg/m^2 has been reported for the city centre in Barcelona (Spain) while mass loadings of 2.4-21.6 mg/m^2 have been reported for different site types across Spain (Amato et al., 2009; Amato et al., 2013). Higher mass loading in Delhi can be attributed to several factors including local meteorology (lower annual rainfall resulting in dry conditions), prevalence of unpaved areas, larger proportion of construction activities, and during the summer season, intrusion of dust from the Thar Desert. The site also had a higher proportion of heavy duty vehicles (HDVs) which could be contributing to the higher mass loading since previous studies have reported higher dust loadings for areas with HDVs (Abu Allaban et al., 2003). Between the road and tunnel sites in Birmingham, elemental concentrations were consistently higher at Site B (UK road tunnel) compared to Site A (UK roadside) with the exception of Al and Si. Elemental concentrations are presented in Figure 1and average mass loadings for elements and organic species are presented in Table S1, SI. Si had the highest concentration among the crustal elements, and Zn, Ti, Ba and Cu were the most abundant traffic-related elements at Sites A and B whereas Zn, Mn, Ti and Ba were the most abundant in the case of Site C. Mass loadings for all the species excluding Sb were found to be higher in the case of Site C (New Delhi) compared to the Birmingham sites (A and B) while the concentrations (μg/g) of elements associated with traffic emissions (i.e. Cu, Zn, Ba, Sb) were found to be highest in the road tunnel environment in

Birmingham (Site B). Previous studies in Houston (USA), by Spada et al. (2012) reported similar results with concentrations of Cu, Zn, Pb, Ba, Sn and Sb found to be higher for bulk RD samples collected in a tunnel compared to roads.

Concentrations of brake wear-related elements such as Sb and Ba in PM_{10} RD were lower in the case of New Delhi compared to Birmingham as well as other European sites while the Ca concentration in Delhi (Site C) was found to be higher than other reported studies. Ca has been used as a marker for crustal dust as well as construction activity (Chen et al., 2012; Pant and Harrison, 2013). In Delhi, previous studies of bulk RD have reported a higher abundance of Ca-rich dust attributed to the dust from the Thar Desert. The concentration of Sn was found to be higher in Birmingham compared to New Delhi. Chemical composition of brakes and tyres is expected to be different in UK and India, and the brake wear mode for elements such as Cu and Sb has not been observed in elemental particle size distributions in New Delhi (Pant et al., 2015 in preparation). For the organic species, concentrations were found to be close to the higher end of the range of the previously reported values. It is important to note that elemental concentrations can vary based on the type of tyres, brakes and pavement used at the site type. For example, summer tyres create a lower dust loading (tyre dust) compared to non-studded and studded winter tyres and both Birmingham and New Delhi use summer tyres all year round (Pant and Harrison, 2013). In addition, concentrations of various crustal elements can vary based on soil type. For example, Fe was found to be 7.4%, 7.3% and 3.1% for Sites A, B and C respectively while Al was found to be 8.7%, 7.2% and 3.98%. Chen et al. (2012) reported the abundance of Fe and Al as 2% and 3.5% in China while Amato et al. (2011) reported Fe abundance of 4.6%, 5% and 5.8% and Al abundance of 2.8%, 8% and 13.6% for Zurich, Barcelona and Girona respectively in the PM_{10} RD.

Based on Pearson correlation analysis (significance at $p < 0.01$), two major groups of elements were identified in the PM_{10} RD in samples from sites A and B (UK roadside and road tunnel), each with statistically significant correlations among the elements in the group. These were crustal elements including Al, Si and Fe (group 1) and traffic-related elements such as Cu, Zn, Sb, Ba, Sn and Mn (group 2). In Beijing (China), Chen et al. (2012) reported four groups: crustal elements (Al, Fe, Ca, Ti), salt (K, Mg, Na), sulphur and other trace elements. At site B, Ni was not found to be correlated to either group. Ni is typically attributed to industrial and fuel oil combustion emissions and has also been attributed to engine metal wear and tear (Hays et al., 2011). Ca showed a high correlation with the traffic-associated elements at Site A. At site C (India roadside), a high correlation was observed between Zn, Cu and Ba but was weaker for Sn, and Sb was not found to be correlated to other traffic-associated elements. Interestingly, while Ti was found to be correlated to traffic-related elements at Sites A and B, a stronger correlation was observed for Ti with Al and Si at Site C. The traffic-related elements could not be subdivided into tyre/brake wear categories based on correlation analysis.

High molecular weight PAHs showed very high correlation with one another, attributable to common sources and deposition pathways.

3.2 Bulk Samples

3.2.1 Soil and road dust

In addition to the PM_{10} RD, bulk soil and road dust samples were analysed to understand the similarities (using Pearson Correlation) in the chemical compositions across the fractions both in UK and India (Figure S3, SI). In the UK, bulk RD (< 2 mm) composition was found to be correlated with bulk soil (< 2 mm) as well as PM_{10} RD while in India, bulk RD (< 2 mm) was found to be correlated with bulk soil (< 2 mm) but the correlation was not significant for PM_{10} RD.

To understand the contribution of traffic emissions to the RD composition (Figure S3, SI), a roadside enrichment factor was calculated based on equation 1 (Amato et al., 2011).

$$Roadside\ Enrichment = \left(\frac{C_r - C_s}{C_r}\right) * 100 \qquad Eq\ (1)$$

Where

C_r is concentration at roadside

C_s is the concentration in soil

Highest enrichment was observed for Ti, Sb and Cr in Birmingham with enrichment of more than 70% while Cu, Zn and Sn showed enrichment of more than 50%. V was not found to be enriched in Birmingham while in Delhi, Sb, Ba and Ni were not found to be enriched. In Delhi, Zn was the only element with an enrichment of > 70% although elements such as Ti, Cu and Sn showed enrichment of more than 30%.

3.2.2 Brake pad and tyre composition

Individual samples of four-wheeler passenger vehicle brake pads from India and UK (one from each country) were analysed to assess the chemical composition. This is particularly relevant in the case of India since there is a need to identify an elemental tracer for brake wear estimation. Pant et al. (2015 in preparation) have highlighted that particle size distributions measured in New Delhi do not show the brake wear modes for elements such as Cu, Sb and Ba which are observed in European samples (e.g. Gietl et al., 2010). However, it is important to note that the sample size is limited, and cannot be used to draw significant conclusions. The differences highlighted using this sample need to be investigated further, and further tests are planned for the next phase of the analysis.

The bulk brake pad dust was found to be rich in Ti (0.12%), Sb (1.12%) and Cu (0.49%) in India, while in the UK, Ba (0.12%) and Sb (0.16%) were the most abundant elements among those analyzed (Figure S4, SI). This is consistent with previous studies in which differences in the composition of brake pads have been reported between different types (e.g. NAO vs low-metallic) (Sanders et al., 2003) and between countries (Kukutschova et al., 2010; Hulskotte et al., 2014). However, it is important that only one sample was analysed per city, and may not be representative of the range of brake pads in use. Future work is underway to further evaluate varying brake pad formulations across geographic regions to understand the chemical composition of brake pads as well as brake wear particles.

In the case of the tyre sample, Zn was found to be the most abundant element (Figure S5, SI).

3.3 Enrichment Factor Analysis for the PM_{10} RD

In order to further understand the sources of the elements (crustal vs. anthropogenic), enrichment factors (EFs) were calculated for PM_{10} RD based on continental crust concentrations using Al as the reference element (Taylor and McLennan, 1995) (Figure).

$$Enrichment\ Factor\ (X) = \frac{\left\{\frac{Concentration(X)}{Concentration(Reference)}\right\}sample}{\left\{\frac{Concentration(X)}{Concentration(Reference)}\right\}crustal} \qquad Eq\ (2)$$

Use of Al as the reference element was based on previous studies in Birmingham that identified a minimal traffic-associated increment for Al (Birmili et al., 2006). Corresponding to the correlations observed in the dataset, highest EFs were observed for Cu, Zn, Sb, Ni and Sn. Across the three sites, Site A (UK roadside) was found to have the lowest enrichment factors. Other studies have

267 also reported high EFs for Ba, Cr, Cu and Sb in airborne particles (Birmili et al., 2006; Dongarra et
268 al., 2009; Oliveira et al., 2011). At the UK sites (Sites A and B), Si, Fe and Ca showed no
269 enrichment with respect to the crustal concentrations; however, Ca was observed to have a high EF
270 at Site C (India roadside). This could be linked with sources associated with construction activity
271 and desert dust which is rich in Ca.

272

273 **3.4 Elemental Ratios in the PM_{10} RD**

274 Ratios between different elements can be used to distinguish between different sources. Various
275 authors have proposed characteristic Cu/Sb ratios for brake wear particles including 4.6 ± 2.3 in
276 USA (Sternbeck et al., 2002) and 7.0±1.9 in Europe (Amato et al., 2009). In comparison, this ratio
277 is 125 for the upper continental crust indicating relatively much higher concentration of Cu in the
278 crust compared to Sb. It is important to note that the Cu/Sb ratio can vary across geographical
279 regions based on the type of brake or the elemental content of the brakes, which differs among
280 manufacturers (Pant and Harrison, 2013; Hulskotte et al., 2014). For example, non-asbestos
281 organic (NAO) brake lining material typically has a Cu/Sb ratio of 11.5 (Iijima et al., 2007) whereas
282 the ratio is 1.33 for semi-metallic brake pad material (Schauer et al., 2006). Recently, Hulskotte et
283 al. (2014) have reported an average ratio value of 4.6 for brake pad material in the Netherlands.

284

285 In the current study, the overall Cu/Sb ratio was observed to be 4.95±0.50 for Site A, 7.50±0.79 for
286 Site B and 11.5±0.82 for Site C. The ratio values for the Birmingham sites fall within the
287 proposed range of characteristic ratios, consistent with a contribution of brake wear particles to
288 the PM_{10} RD, and are similar to the Cu/Sb ratio of 7.5 reported for low-metallic brake pads in
289 the USA (Schauer et al., 2006). However, a higher ratio (11.5) was observed in the case of Site
290 C (India) which could be due to either other sources of Cu in the area, or due to differences in the

composition of brakes. For the bulk RD, the Cu/Sb ratio was 4.80±0.40 for Delhi and 6.22±3.16 for Birmingham.

Further discussion on elemental ratios is presented in SI.

3.5 Chemical Source Profiles of the PM_{10} RD

Source profiles (weight % of species with respect to the mass of PM) were generated for the road traffic sites in Birmingham (Sites A and B) and New Delhi (Site C) and appear in Table 1 (see Table S2 in SI for other molecular markers).

Previously reported source profiles for RD and various non-exhaust emission sources were compared against data obtained at Sites A-C in order to achieve a qualitative understanding of source contributions (Figure 3).

The source profiles were extracted from the USEPA SPECIATE 4.3 database and other published literature. In the case of elements, profiles included paved RD [highway (profile number 3565), tunnel (profile number 4112410)] and RD (Mexico) (profile number 4106), from the SPECIATE database, paved RD from India (Sethi and Patil, 2008), Hong Kong (Ho et al., 2003), Barcelona (Amato et al., 2009) and Beijing (China) (Chen et al., 2012). Concentrations of various elements were broadly similar to other compositional profiles of PM_{10} RD, and in most cases, PM_{10} RD concentrations in the tunnel were higher than roadside samples. A previously reported compositional profile of PM_{10} RD for Delhi (Sethi and Patil, 2008) was found to be different from the current profile. Concentrations of several elements including Si, Al, Ca and Ba were much lower in the case of the profile from Sethi and Patil (2008), while concentrations were lower for the current profile for Sn, OC and EC and comparable for Ti, Fe and Zn. The Si/Al ratio was found to be lower than the UCC value of 3.9 for the profile from Sethi and Patil (2008) while the Cu/Sb ratio

317 at 21.5 was much higher compared to the profile generated in this study. The OC/EC ratios were,
318 however, comparable (3.6 for current study, 3.3 for Sethi and Patil, 2008).

319

320 **3.6 Source Apportionment**

321 Recently, a novel method was proposed for the estimation of source contributions of non-exhaust
322 sources using Ba, Zn and Si as source markers for brake dust, tyre dust and crustal dust respectively
323 (Harrison et al., 2012). The factors reported by Harrison et al. (2012) (91 for Ba, 50 for Zn and 3.6
324 for Si) were used to convert masses of these elements to mass contributions of brake dust, tyre dust
325 and crustal dust respectively to the total PM_{10} mass (Table 2 and Figure S6, SI). It is important to
326 note that Zn is emitted from various sources which include engine emissions and brake dust, and it
327 is possible that using Zn as a tyre wear tracer results in an over-estimation of the tyre dust
328 emissions. In Asia, Zn has also been associated with 2-stroke gasoline engine emissions and
329 emissions from the galvanization industry (Begum et al., 2011). Further, preliminary analysis of
330 brake pad samples from New Delhi (Section 3.2) reveals that levels of Ba are quite low in the brake
331 pads in New Delhi. In the case of New Delhi, Fe was used as the source marker for crustal dust
332 due to its high abundance in crustal material. In addition, a factor of 1.35 was used for EC to
333 estimate the contribution of vehicular exhaust (Pio et al. 2011).

334

335 Application of these factors accounted for a high proportion of PM_{10} RD mass in the UK samples
336 (99.3% for Site A and 105% for Site B), with the highest contribution from crustal dust. For site B
337 (road tunnel), the contribution of tyre wear was calculated to be 15.6% which might be an over-
338 estimation since Zn is emitted from other sources as well. The contribution of brake wear was
339 also the highest for Site B. In the case of Delhi, 79.2% of the total mass is accounted for by this
340 method but if Si is used as the source marker for crustal dust, only 51% of the total PM_{10} mass is
341 estimated. This indicates that this estimation method cannot be used universally, and it is important

to adjust the markers/factors according to the local soil characteristics. Other sources which could make important contributions in the case of New Delhi are construction activity and deposition from other sources which are currently not included in the estimation. Vehicle exhaust was found to contribute a very small percentage to the total PM_{10} mass which is plausible since most of the vehicle exhaust particles are in the smaller size fraction and are less likely to deposit.

Chen et al. (2012) estimated soil dust, construction-related particles, vehicle exhaust, particle deposition and coal burning-associated particles as the key sources for RD in Beijing. Further evaluation of brake wear, tyre wear, crustal dust and vehicle exhaust by Amato et al. (2013) demonstrated these emission sources contributed 27%, 16%, 37% and 20%, respectively of the total PM mass in Barcelona and 39%, 41%, 12%, 8%, respectively, in Utrecht, the Netherlands.

To compare the attribution of crustal dust using Si against an independent estimate, crustal dust mass was reconstructed using the concentrations of Al, Si, Fe, Ca and Ti using the equation (3) (Chan et al., 1997). Results indicated good correlation between measured and reconstructed mass in all cases with $r^2 > 0.85$ in all cases. However, as with the source apportionment, the amount of mass apportioned as crustal dust was observed to be low at Site C (Indian roadside). This may be related to the varied soil composition at different locations. Hence, it can be concluded that it is important to analyse uncontaminated soil samples (bulk and PM_{10} fraction where possible) to determine the local chemical composition which can be then be used to adjust the crustal dust factor.

$$Crustal\ Dust\ =\ 1.16\ (1.90\ Al +\ 2.15\ Si +\ 1.41\ Ca +\ 1.67\ Ti +\ 2.09\ Fe) \qquad Eq\ (3)$$

365 **3.7 Oxidative Potential**

366 While it is well known that PM exposure is a contributor to adverse cardiopulmonary health, the
367 hazards posed by PM emitted from different sources may vary dependent upon the characteristics of
368 the emitted particles. Particle toxicity is thought to vary based on chemical composition. Specific
369 constituents of PM such as redox active trace metals (e.g. Cu, Zn, Ni) and PAHs may be
370 particularly harmful as they can lead to the generation of reactive oxygen species (ROS) and
371 subsequent inflammation and oxidative stress (Kelly, 2003; Ayres et al., 2008). Multiple PM
372 constituents have been shown to exert Oxidative Potential, which may lead to oxidative stress in
373 biological systems, and Oxidative Potential has been suggested as a biologically informative
374 expression for response assessment (Weichenthal et al 2013). Recent studies of PM have
375 highlighted the high Oxidative Potential of non-exhaust road traffic emissions (Godri et al., 2011;
376 Kelly et al, 2011; Yanosky et al., 2012; Janssen et al 2014; Amato et al., 2014). The oxidative
377 potential (OP) of a subset of bulk and PM_{10} RD samples was measured in the current study.

378

379 Both OP associated with ascorbate depletion per unit PM mass (OP^{AA}) and OP associated with
380 glutathione depletion per unit PM mass (OP^{GSH}) were found to be higher for the bulk RD compared
381 to the PM_{10} RD (Figure 4). OP^{AA} and OP^{GSH} were not found to be correlated with each other,
382 suggesting that distinct chemical species were contributing to the depletion of each antioxidant.
383 This result supports previous studies that have shown that glutathione and ascorbate respond to
384 different chemical components of PM (Godri et al., 2010a; Kelly et al., 2011).

385

386 Published studies have shown significant associations between OP and transition metals in ambient
387 PM_{10} samples, specifically the recurring correlation between OP^{GSH} and Fe (Godri et al., 2010a;
388 Kelly et al., 2011; Godri et al., 2011). Yang et al. (2014) and Janssen et al. (2014) also found
389 significant positive associations between Fe, Cu and OP^{AA} for $PM_{2.5}$ while Godri et al. (2010b)

found positive association between Fe, Pb and OP^{AA} for PM_{10}. Fe and Cu are traffic related redox active transition metals thought to drive antioxidant depletion (Kelly et al. 2011). Linear regression analysis was performed to understand the contribution of individual elements to the oxidative potential. For OP^{GSH}, no significant relationships were observed for either PM_{10} or bulk RD. On the other hand, OP^{AA} showed some significant relationships for both fractions ($p < 0.05$). In terms of individual elements, Cu was the only significant element ($r^2 = 0.995$, $p = 0.044$) for bulk RD (Figure S7, SI) while for PM_{10}, Ti ($r^2 = 0.54$), Mn ($r^2 = 0.52$), S ($r^2 = 0.57$), As ($r^2 = 0.55$), Cu ($r^2 = 0.61$) and V ($r^2 = 0.57$) were found to be significant for $p < 0.05$ (Figure S8, SI). Results of the regression analysis are summarized in Table 3. Cu is typically associated with non-exhaust traffic emissions (Amato et al., 2009; Pant and Harrison, 2013), and was found to be associated with OP^{AA} in both fractions of RD. On the other hand, Mn, V and Ti can be associated with traffic as well as other sources such as fuel oil combustion. It is useful to note that at Site A (UK roadside), high correlations were observed between elements. Interestingly, Fe and Zn were not found to be a significant in the regression models for either of the RD fractions.

4. CONCLUSIONS

Non-exhaust particles constitute an important source of PM emissions in urban areas, and the chemical composition as well as contribution can vary from region to region. Since there are a number of contributions to non-exhaust emissions, it is often difficult to estimate the contribution of different sources to RD. In this study, an attempt was made to undertake detailed characterization of the PM_{10} RD and the empirical method proposed for estimation of the contribution of non-exhaust sources was applied with some success to the dataset.

Chemical source profiles generated for the PM_{10} RD at sites in Birmingham and New Delhi correspond well with previously reported RD profiles, although differences were observed between

element concentrations in UK and India. This can be attributed to the difference in soil composition as well as the chemical composition of tyre and brake pads. Comparison carried out between elemental and PAH ratios for RD PM and airborne PM reveal that the ratios can be quite similar between RD and ambient PM, particularly in the case of coarse PM.

The empirical factors generated by Harrison et al. (2012) relating tracer elements to particle mass were found to be able to account well for source contributions in the area where they were empirically determined (i.e. high traffic areas in UK), but these factors were not able to apportion all the PM mass for the Indian site. Low mass closure in New Delhi is perhaps due to the different sources that influence the dust concentrations in New Delhi, as well as due to differences in the overall concentrations of different elements, and perhaps their sources as well. It is therefore necessary to adjust the factors before using them for analysis in other regions. The estimated contribution of brake wear was very similar between Sites A (UK roadside) and C (Indian roadside), both of which experience heavy-trafficked roads with stop-and-go traffic flows.

The dataset generated in this study will be useful in receptor modelling studies. It is critical to note that the contribution of non-exhaust emissions to ambient PM concentration varies based on site characteristics, and data generated with pilot studies in specific areas/site types cannot be used to generalize the role and quantitative contribution of non-exhaust emissions to ambient air quality.

A preliminary assessment of the Oxidative Potential of RD (bulk and PM_{10}) has been made in this study. Cu, often used as a traffic emissions marker, was found to be significant in both cases. However, it is important to note that multiple metals are redox active, and can lead to antioxidant depletion (Godri et al., 2011), and it is possible that the complex interactions are not completely expressed through this limited dataset. Further analysis is required to understand the drivers for the

differences across sample fractions (PM_{10} vs. bulk) and to quantify the health risks associated with exposure to non-exhaust emissions vis-à-vis other emission types.

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TABLE LEGENDS

Table 1: Chemical source profiles for heavy traffic sites in Birmingham (Sites A and B) and New Delhi (Site C) (% w/w).

Table 2: Source contributions of various non-exhaust sources to the PM_{10} fraction of road dust in Birmingham and Delhi (in %).

Table 3: Parameters of the regression model to explain oxidative potential variance for road dust (more significant outcomes only).

FIGURE LEGENDS

Figure 1: Concentrations of various elements in the PM_{10} fraction of road dust at Sites A-C (µg/g).

Figure 2: Enrichment factors for sites A-C.

Figure 3: Comparison of species concentration (weight %) observed in the current study with the PM_{10} fraction of road dust sampled elsewhere.

Figure 4: Oxidative Potential (OP) per µg dust for the PM_{10} fraction and bulk road dust samples for site A.

757 **Table 1**: Chemical source profiles for heavy traffic sites in Birmingham (Sites A and B) and New
758 Delhi (Site C) (% w/w)

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Species	***Site A***		***Site B***		***Site C***	
	Conc.	**SD**	**Conc.**	**SD**	**Conc.**	**SD**
OC	7.91	4.80			1.82	1.69
EC	0.13	0.41			0.51	0.29
Si	28.8	17.6	28.2	8.98	13.0	3.04
Al	8.66	4.81	7.22	2.34	3.98	1.04
Ca	3.24	1.62			5.00	0.64
Fe	7.39	8.92	7.32	2.00	3.11	0.49
Ti	0.032	0.025	0.078	0.029	0.047	0.005
Mn	0.044	0.037	0.077	0.025	0.044	0.005
Cu	0.035	0.029	0.108	0.032	0.016	0.002
Sb	0.007	0.006	0.014	0.003	0.001	0.000
Ba	0.033	0.027	0.087	0.027	0.042	0.005
Sn	0.005	0.004			0.001	0.000
Cr	0.007	0.006	0.017	0.007	0.006	0.001
V	0.002	0.002	0.005	0.002	0.003	0.000
Zn	0.071	0.058	0.366	0.142	0.068	0.009
Ni			0.012	0.009		
S	0.11	0.18	0.99	0.29		
Benzo(b)fluoranthene (BbF)	0.004	0.002			0.004	0.003
Benzo(k)fluoranthene (BkF)	0.004	0.002			0.003	0.002
Benzo(e)pyrene (BeP)	0.003	0.002			0.002	0.001
Benzo(a)pyrene (BaP)	0.002	0.001			0.002	0.002
Indeno(123-cd)pyrene (IcdP)	0.002	0.001			0.002	0.002
Benzo(ghi)perylene (BghiPe)	0.002	0.001			0.002	0.002
Coronene (Cor)	0.001	0.000			0.001	0.000

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762 **Table 2**: Source contributions of various non-exhaust sources to the PM_{10} fraction of road dust in
763 Birmingham and Delhi (in %)

Site ID	***Site characteristics***	***Brake Wear (Ba)***	***Tyre Wear (Zn)***	***Crustal Dust (Si/Fe)***	***Vehicle Exhaust***	***Total Mass Estimated***
Site A	High traffic volume, stop-and-go traffic, mixed LDVs and HDVs	3.8	4.7	89.5	1.3	**99.3**
Site B	High traffic volume, smooth traffic flow with stop-and-go during congestion, mixed LDVs and HDVs	6.6	15.6	82.8	-	**105**
Site C	High traffic volume, stop-and-go traffic, mixed LDVs and HDVs Open unpaved area in vicinity	3.9	3.5	71.2	0.59	**79.2**

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Table 3: Parameters of the regression model to explain oxidative potential variance for road dust (significant outcomes only)

Sample type	*Metric*	*Metal (µg/g)*	*Explanatory Variable*		*Model*		
			Slope	**Intercept**	**R^2**	**SE**	**p-value**
Bulk RD (<2mm)	OP^{AA} μg^{-1}	Cu	6019 ± 416.4	-668 ± 52.7	0.995	4.40	0.044
PM_{10} RD	OP^{AA} μg^{-1}	Cu	2363 ± 768	4.28 ± 45.6	0.61	32.2	0.022
(<10 µm)		Ti	5460 ± 2076	-57.4 ± 123	0.54	86.9	0.039
		V	331 ± 118	-4.04 ± 7.03	0.57	4.96	0.031
		Mn	4214 ± 1643	-19.7 ± 97.5	0.52	68.8	0.043
		As	64.8 ± 23.9	-0.93 ± 1.42	0.55	1.00	0.035
		S	86326 ± 30757	-2705 ± 1825	0.57	1288	0.031

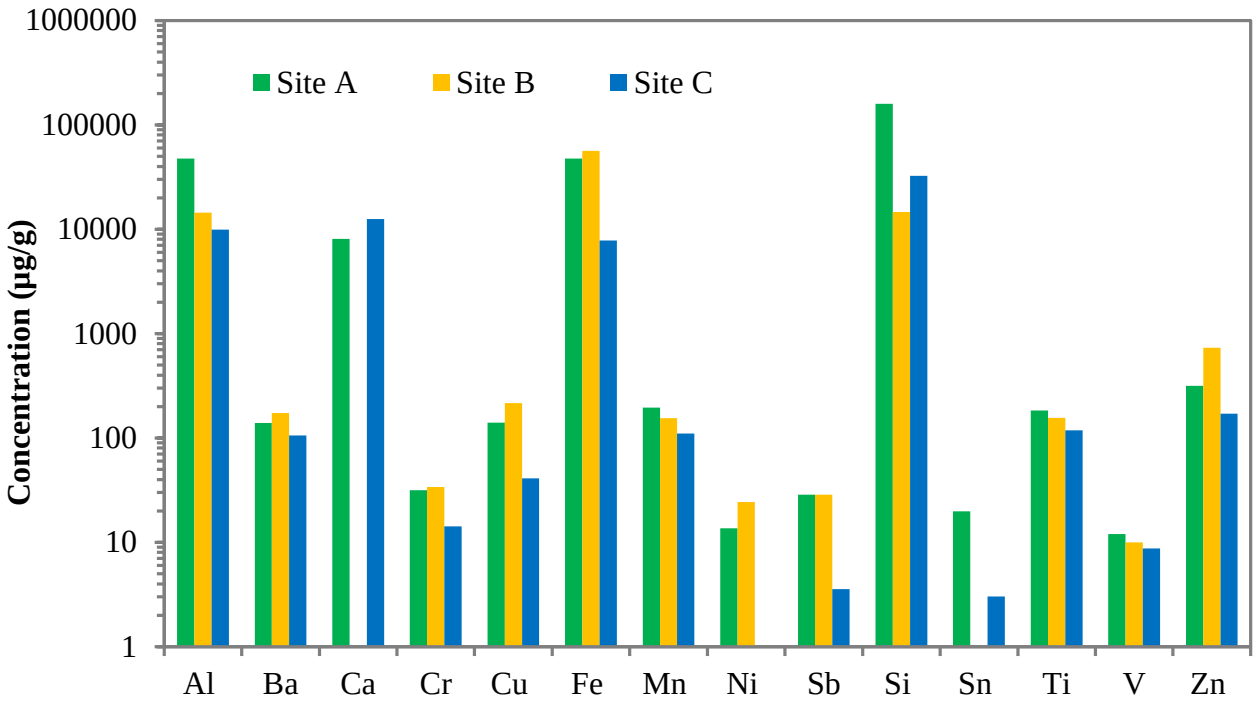


Figure 1: Concentrations of various elements in the PM_{10} fraction of road dust at Sites A-C (µg/g) (Site A- UK roadside, Site B- UK tunnel and Site C- India roadside).

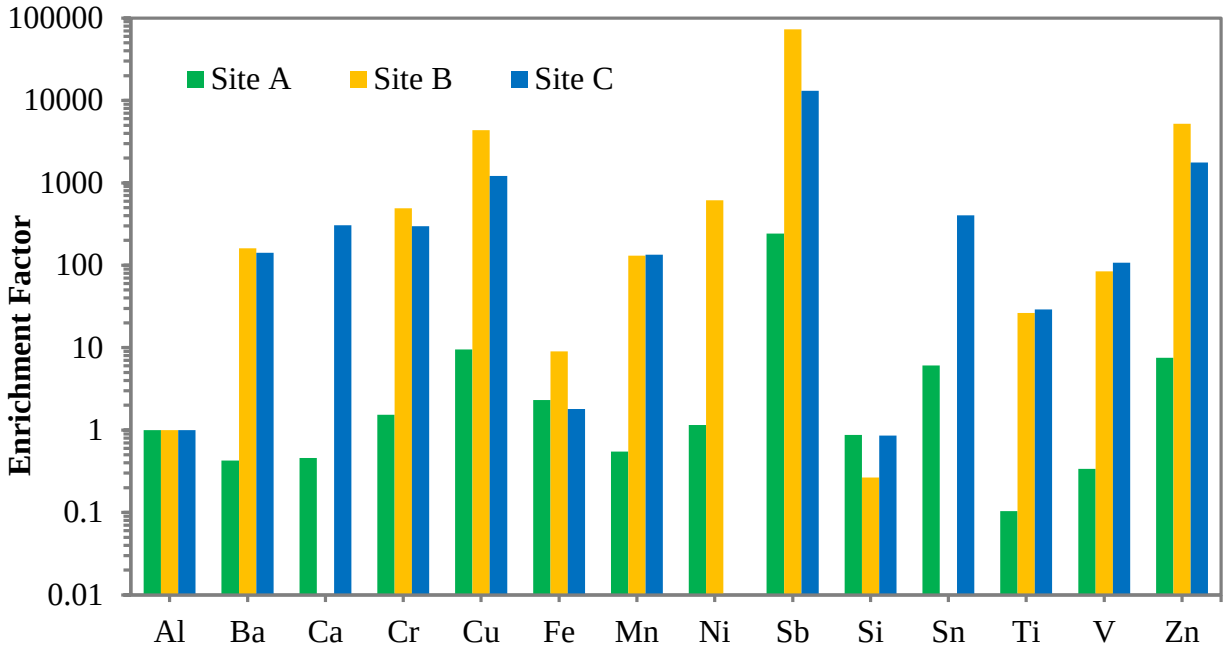
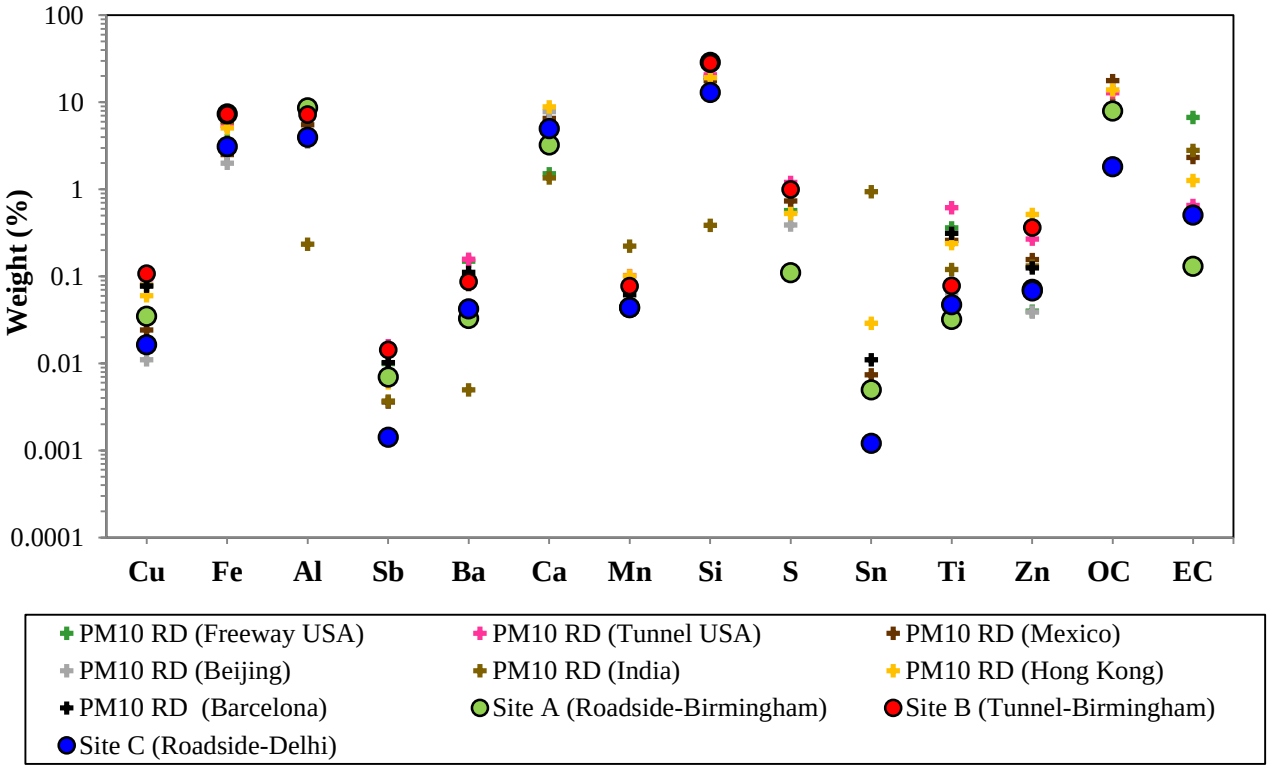


Figure 2: Crustal enrichment factors for sites A-C.



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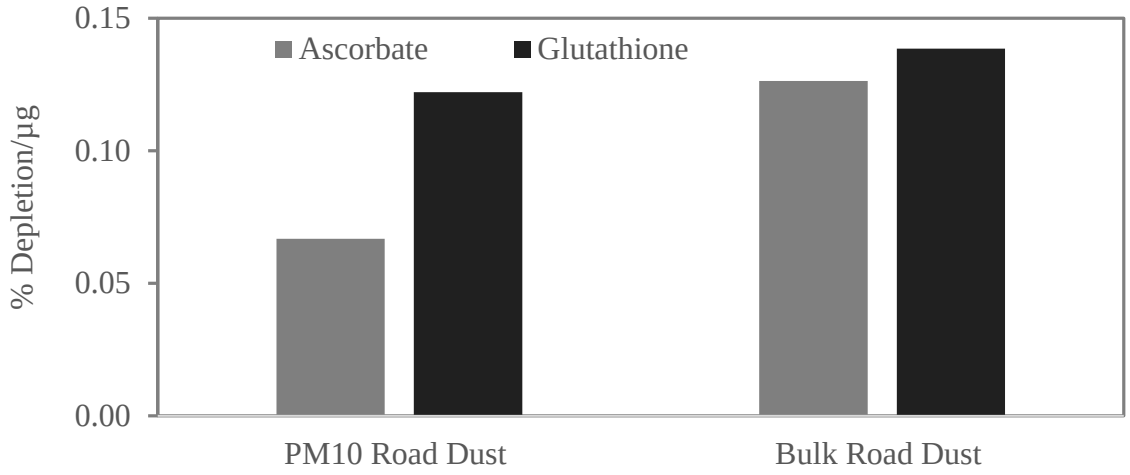
784 **Figure 3:** Comparison of species concentration (weight %) observed in the current study with the
785 PM_{10} fraction of road dust sampled elsewhere.

786



787

788 Figure 4: Oxidative Potential (OP) per µg dust for the PM_{10} fraction and bulk road dust
789 samples for site A.
790